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13. ABSTRACT (Maximum 200 words) Block copolymer architectures containing both rigid-rod and flexible-coil blocks have novel self-organizing features and functional properties not possible with coil-coil architectures. We describe the self-assembly of new rod-coil diblock, rod-coil-rod triblock, and coil-rod-coil triblock copolymers from solution and the resulting discrete and periodic mesostructures with sizes in the 100 nanometer to 200 micrometer range. For example, hollow microspheres, cylindrical microtubules, disc-like lamellae, and doughnut shaped discrete objects self-organized from polyquinoline-b-polystyrene diblocks in a selective solvent for the polyquinoline[1a]. However, the same rod-coil diblock copolymers in a selective solvent for the polystyrene form hollow spheres which self-order into periodic mesoporous materials[1b]. The roles of macromolecular architecture and competing intermolecular interactions on the self-organized mesostructures will be shown.[1](a) Jenekhe, S. A.; Chen, X. L. Science 1998, 279, 1903-1907; (b) Science 1999, 283, 372-375.				
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Self-Assembly of Rod-Coil Block Copolymers

By

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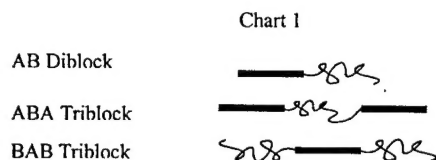
SELF-ASSEMBLY OF ROD-COIL BLOCK COPOLYMERS

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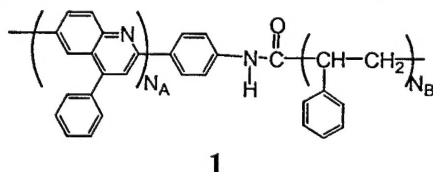
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Introduction

Block copolymer architectures containing both rigid-rod and flexible-coil blocks (chart 1) can have novel self-organizing features and functional properties not possible with all-coil architectures.¹⁻⁴ The anisotropic molecular shape and stiff rodlike conformation of the rod block imparts orientational self-ordering (mesophase formation), chain stiffness, and interactional asymmetry between the blocks of rod-coil block copolymers. The expected competing interactions in such multicomponent polymer systems could be a basis for achieving self-organization over many length scales from the nanometer level to the macroscopic.³ Although some theoretical studies of rod-coil block copolymers have been reported,⁴ the level of theoretical and experimental understanding of their phase behavior, self-assembly, and self-organized mesostructures is still very rudimentary compared to coil-coil systems. Most of the experimental rod-coil block copolymers investigated to date have been those containing helical rods.⁵



We describe the self-assembly of new rod-coil block copolymers from solution, including AB rod-coil diblocks, ABA rod-coil-rod triblocks, and coil-rod-coil triblocks (Chart 1), and the resulting discrete and periodic mesostructures. A specific example is poly(phenylquinoline)-*block*-polystyrene (PPQ-*b*-PS, **1**) whose molecular structure is shown below. Our



initial results on the self-assembly of **1** from a selective solvent for the PPQ block have been reported.¹ The unusual hierarchical self-assembly of periodic microporous materials from **1** in a selective solvent for PS has also been reported.² We have found that discrete mesoscopic (100 nm to 200 μ m) objects such as hollow spheres, cylindrical tubules, disc-like lamellae, and doughnuts self-organized from **1** and PPQ-*b*-PS-*b*-PPQ triblock (**2**). Interestingly, **1** was able to solubilize and encapsulate large quantities of fullerenes C₆₀ and C₇₀.^{1,7} By employing conjugated rodlike blocks such as PPQ, which is well-known to have electronic, optoelectronic, and photonic properties, such as electrical conductivity when doped,⁸ electroluminescence,⁹ third order nonlinear optical effects,¹⁰ electrochemical redox activity,¹¹ and photoconductivity,¹² we hope to build various functionalities into supramolecular assemblies of rod-coil block copolymers. Novel cooperative or collective properties not found in the component conjugated polymers are also anticipated in such electroactive and photoactive supramolecular assemblies of rod-coil block copolymers. Also of fundamental interest to the emerging field of *supramolecular polymer science* is that the electroactive and photoactive building blocks facilitate new ways of characterizing the self-assembly, molecular packing, aggregate morphology, and dynamics of macromolecular self-assembling mesostructures by optical and photoelectronic techniques.^{1,2,6,7}

Experiments

The synthesis, purification, and structural characterization of all the rod-coil block copolymers are described elsewhere.^{1,6} Among compositions of diblocks **1** whose self-assembling properties are described here are 50-*b*-300 (**1a**), 10-*b*-300 (**1b**), 10-*b*-1000 (**1c**) and 50-*b*-2000 (**1d**). Samples of the rod-

coil-rod triblock **2** include 50-*b*-500-*b*-50 (**2a**), 50-*b*-250-*b*-50 (**2b**), and 50-*b*-120-*b*-50 (**2c**). Analytical grade solvents trifluoroacetic acid (TFA), dichloromethane (DCM), toluene, and carbon disulfide (CS₂) from Aldrich were used as received. Fullerenes C₆₀ (TCI, 99.9 %) and C₇₀ (Aldrich, 99 %) were used as received. Various volume ratios (e.g. 4/1, 2/1, 1/1, 1/4) of TFA/DCM or TFA/toluene binary mixtures were found to be excellent selective solvents for the rodlike PPQ block. CS₂ was a selective solvent for the PS block in the diblocks **1**. Solutions of diblock or triblock copolymer in TFA/DCM or TFA/toluene had concentrations in the range of 0.01 to 0.5 wt % (ca. 0.07 to 3.5 mg/mL).

Self-assembled aggregates of rod-coil block copolymers were dried on a substrate in air at various temperatures (20 to 90 °C) and examined by optical, fluorescence, and electron microscopies and by optical absorption and photoluminescence (PL) spectroscopies.

Results and Discussion

Some of the typical self-assembled aggregates of rod-coil diblock copolymer **1a** from a rodlike block selective solvent (TFA/dichloromethane) are shown in Figure 1. Multiple morphologies including spheres, disc-like lamellae, and cylinders were observed as the self-organization temperature and solvent composition were varied. The polymorphism of the micelle-like aggregates obtained from diblocks **1** under different conditions (solvent composition, temperature) suggests that competition among the significant intermolecular interactions (solvophobic, screened electrostatic, van der Waals, and hydrogen bonding) is a key feature in the self-assembly process of the present rod-coil block copolymers. Two remarkable features of these micellar aggregates are their robustness and sizes. For example, the aggregates were repeatedly heated to 200 °C which is above the glass transition (*T*_g) of PS blocks (~100 °C) but less than that of PPQ blocks (>350 °C) without deassociation or change in aggregate morphology.^{1,6} The size scale of the self-organized discrete objects from diblocks **1** is up to 10-100 μ m, making them comparable to self-assembled mesostructures in cellular biology.

Dissolution of triblocks **2** in TFA/DCM mixtures of various ratios (TFA/DCM = 9/1 to 1/9) at room temperature (25 °C), without sonication or other forms of applied energy, resulted in the spontaneous self-assembly of vesicles (hollow spheres) exemplified in Figure 2. Only *spherical vesicles* of various sizes were self-organized from all the rod-coil-rod triblock copolymers **2** and the different conditions (solvent composition, concentration, and temperature) investigated. This result is in sharp contrast to the multiple morphologies of aggregates self-organized from the related diblock copolymers **1**. This demonstrates the control of the three-dimensional (3-D) shape of molecular assemblies through macromolecular architecture. The diameter of vesicles of **2** was in the range of 100 nm to 200 μ m; the average diameter decreased with decreasing molecular weight of the PS blocks.

We have found that whereas fullerenes C₆₀ and C₇₀ are insoluble in pure TFA, or TFA/DCM or TFA/toluene, they readily dissolved in the mixed protic solvents containing a diblock **1** at room temperature (25 °C). Extensive studies of the solubilization and encapsulation of fullerenes by these rod-coil diblock copolymers have shown that fullerene solubilization in DCM and toluene is enhanced by factors of 60 to 1000, the aggregation number is increased to over 10⁹ chains/aggregate, and up to 10⁷ to 10¹⁰ fullerene molecules can be encapsulated per micellar aggregate.⁷ The resulting fullerene/block copolymer assemblies represent new supramolecular materials with potential electronic, optoelectronic, and nonlinear optical properties.

Conclusions

Our studies of new rod-coil block copolymers have discovered novel supramolecular self-assembly features and self-organized mesostructures with size scale in the 100 nm to 200 μ m range. The self-organized discrete objects are the largest outside of living systems. In the case of rod-coil diblock copolymers, they have been observed to undergo hierarchical self-assembly in a selective solvent for the coil block to periodic mesoporous materials.² In a selective solvent for the rodlike block the same diblocks have solubilized and encapsulated millions and billions of fullerene molecules.^{1,7}

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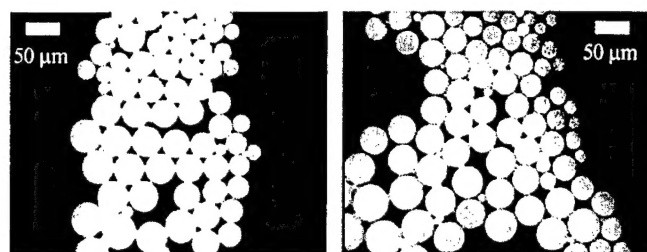


Figure 2. Fluorescence photomicrographs of vesicles self-assembled from triblock **2a** in TFA/dichloromethane solutions.

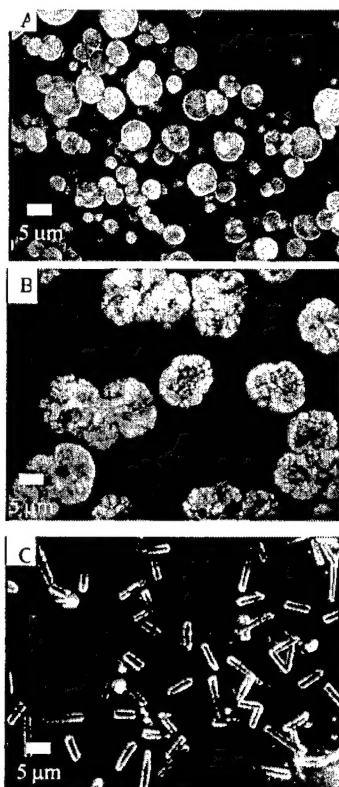


Figure 1. Fluorescence photomicrographs of micellar aggregates of diblock **1a** from TFA/dichloromethane solutions.